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Mathews, Haddan & Co.(54) Solid electrolyte cells for gas
analysis

(57) Apparatus for simultaneous analysis of different gases consists of a hollow solid electrolyte body surrounded by two or more measuring electrodes 2, 21 with corresponding conductor wires fastened to the body in grooves of guide tube 13 and secured by a multiple capillary tube plus bolt or corrosion proof element. The body is coaxially sealed, gas-tight, to the guide tube with glass or a sintered composition and these, together with gas conduit 41, optional ceramic heater tube 44 and thermocouples 40, 43, are mounted

within porous ceramic tube 34 which acts as a filter and may have opening 51. Solid reference electrodes are mounted within the electrolyte tube adjacent the measurement electrodes. The apparatus may continuously monitor O_2 , SO_2 , NO_2 or CO_2 concentration and respective suitable electrolytes are ZrO_2 or a salt of one of the other gases impregnated into Al_2O_3/SiO_2 or Al_2O_3/MgO mixtures or in windows in sintered corundum. Respective reference electrodes for the gases other than oxygen are mixtures, of, alkali-free salts of the gases and 1% of a silver salt of appropriate gas, coated on silver.

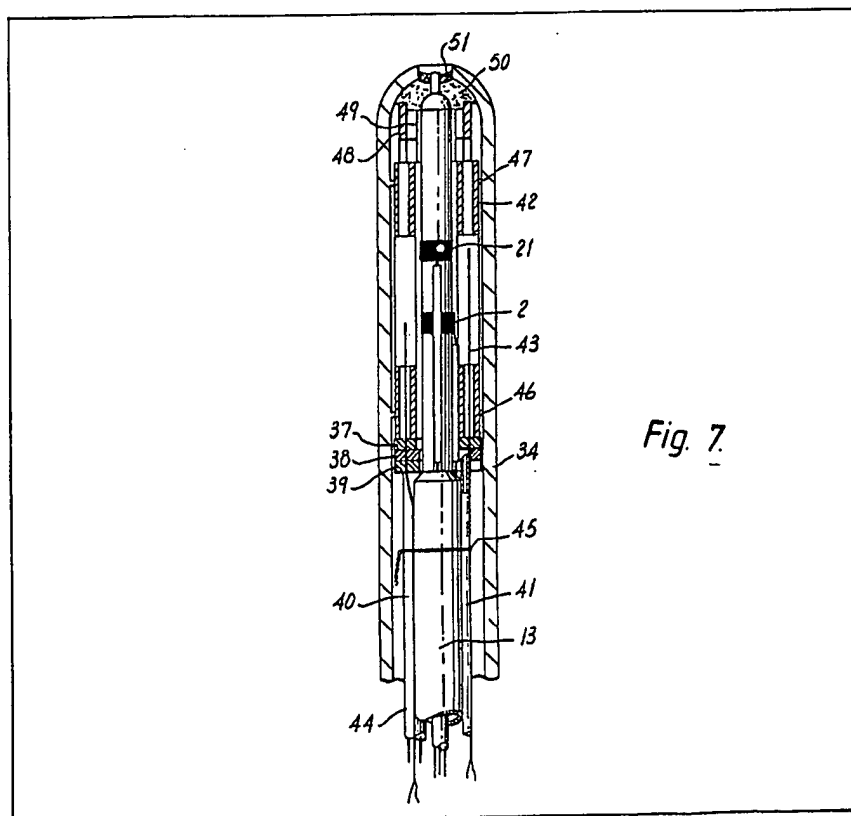


Fig. 7

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

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Fig. 1.

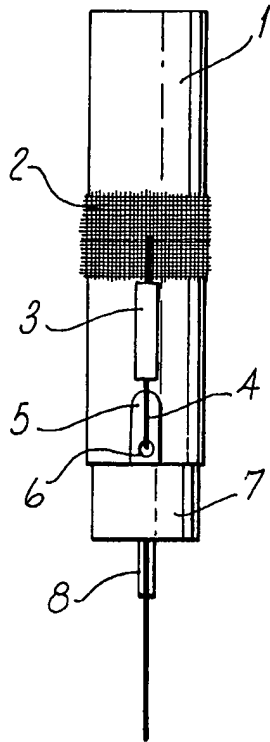


Fig. 1a.

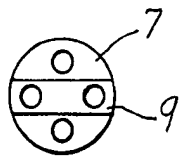
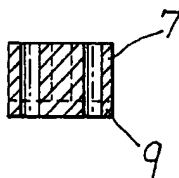


Fig. 1b.



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Fig. 2.

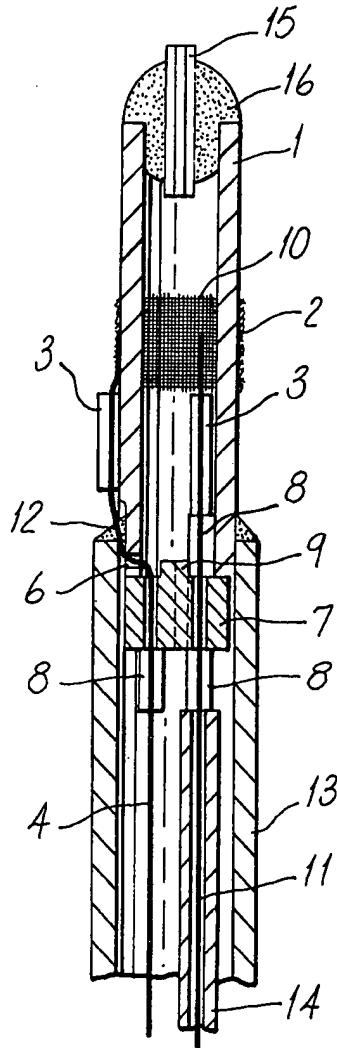


Fig. 3.

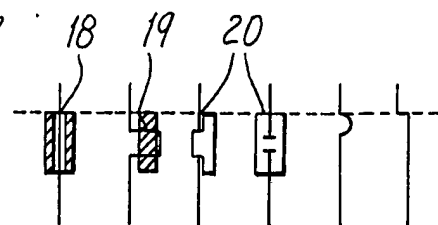
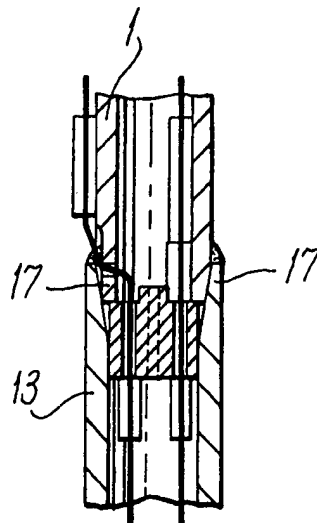
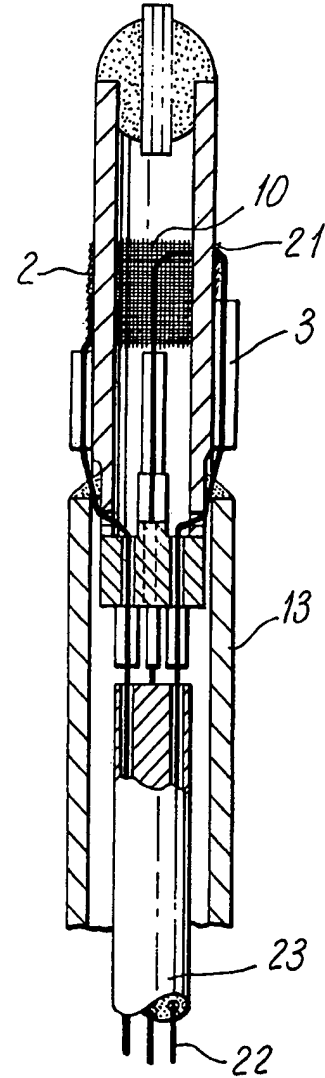


Fig. 2a. 2b. c. d. e. f

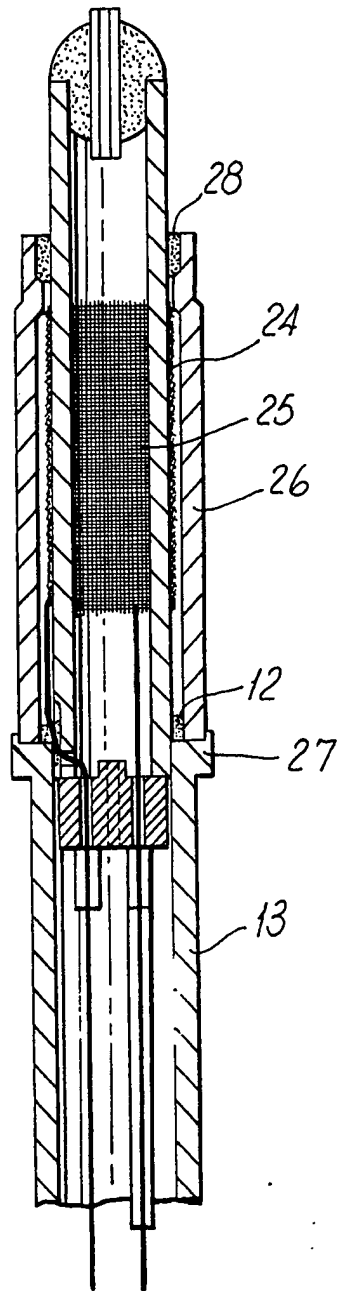


Fig. 4.

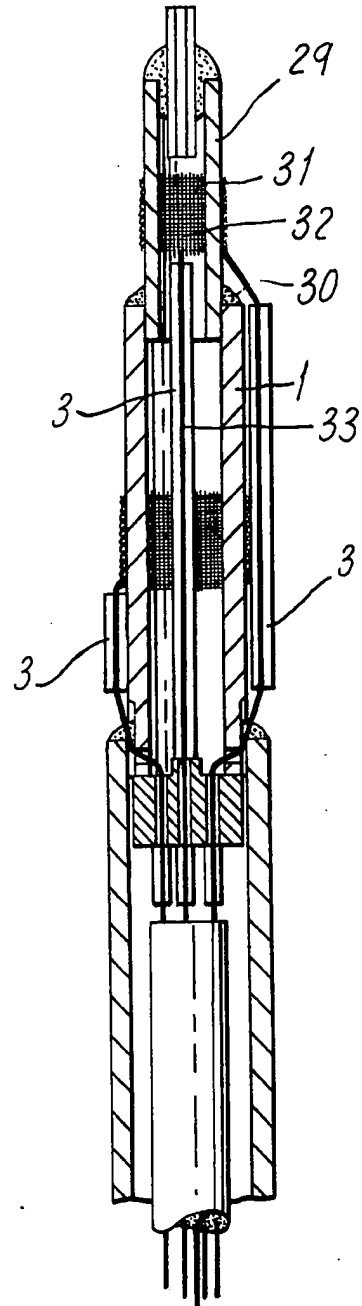


Fig. 5.

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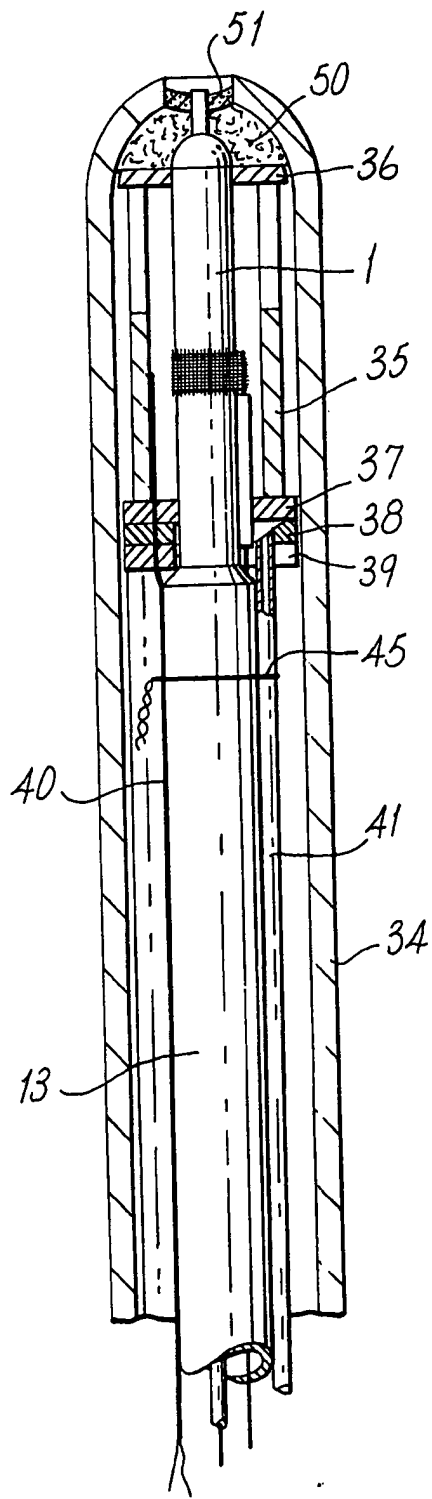


Fig. 6.

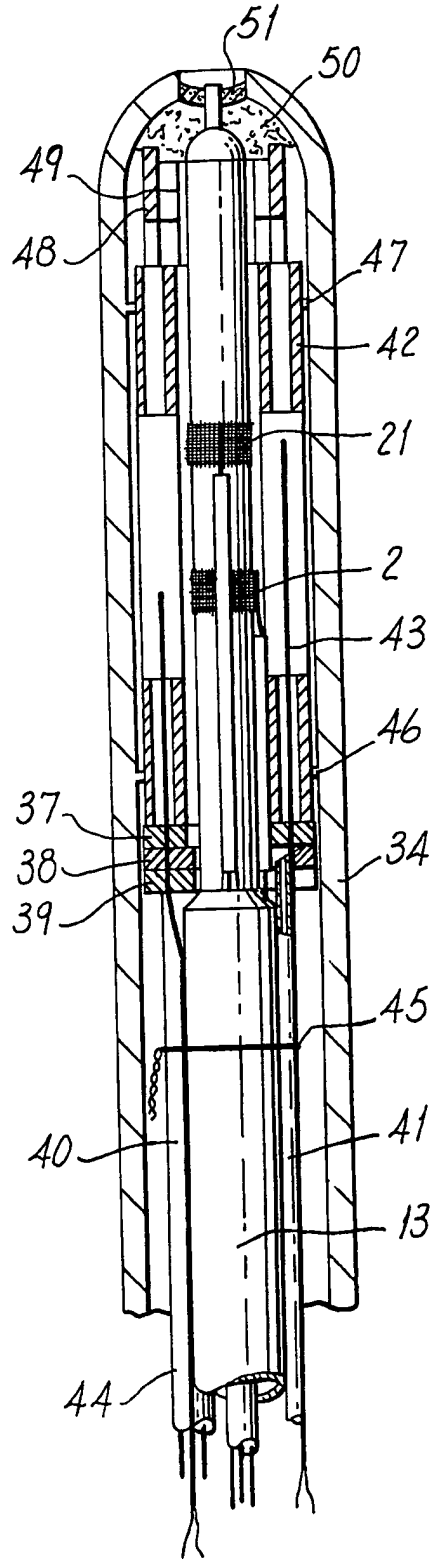
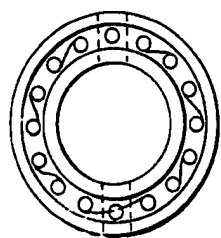
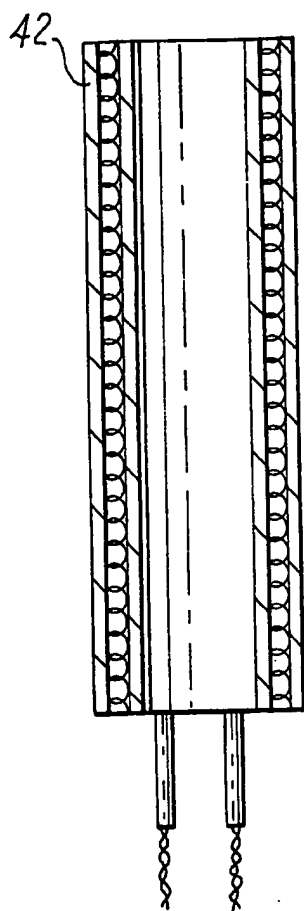
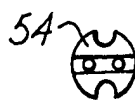
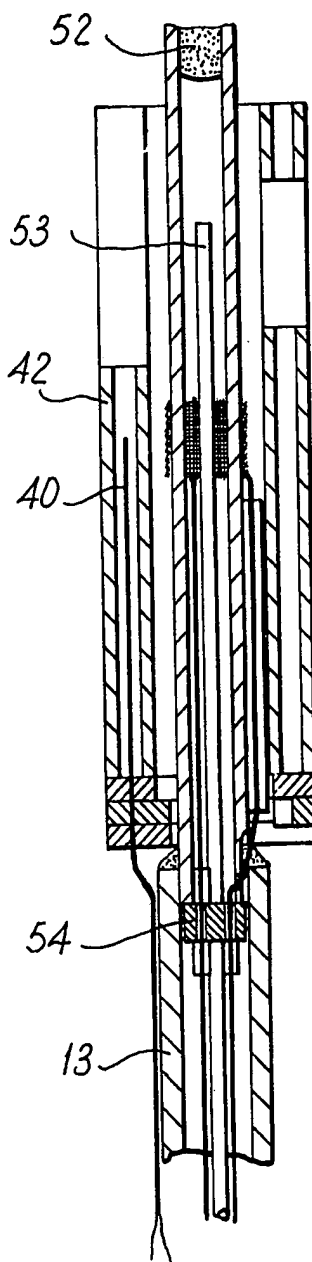
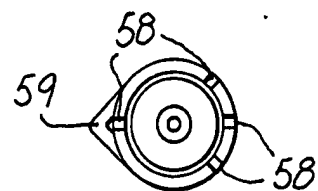
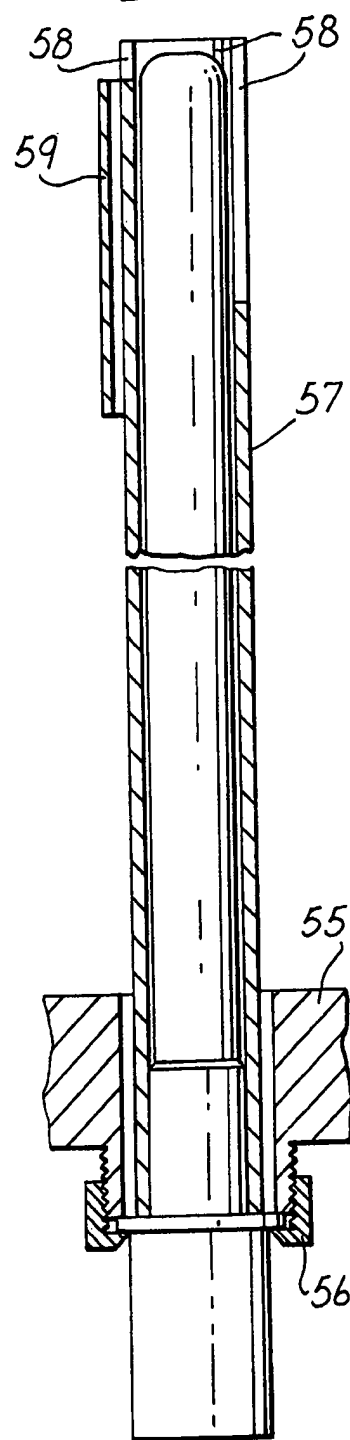


Fig. 7.

Fig. 8.*Fig. 8a.**Fig. 9.**Fig. 9a.**Fig. 10a.*

SPECIFICATION

Apparatus for gas analysis with galvanic solid electrolyte cells

5 The invention relates to an apparatus for gas analysis with galvanic solid electrolyte cells which is usable for monitoring, control and regulating purposes especially on industrial gases and in air and can be used, exploiting potentiometric, ammetric and coulometric methods and catalytic effects, in each case with minor modification, for different individual or several simultaneous continuous determinations, especially of oxygen, sulphur dioxides, nitrogen oxides and carbon dioxide, and for the detection of unburned gases
10 beside oxygen. The apparatus constitutes a basic conception for various kinds of solid electrolyte gas sensors. 10

The development of the scientific field of high temperature electrochemistry with solid electrolyte cells has led to the discovery of numerous solid electrolytes and to the development of various arrangements and methods with solid electrolyte cells which are suitable in a wide temperature range for the continuous or
15 discontinuous selective determination of individual components of pure and impure gas mixtures. These apparatuses are distinguished in that they directly deliver electric signals which can be fed simply to electronic display and recording appliances or automatic regulators. The introduction of probes with the measurement position in the probe head directly into the industrial gas current to be examined is especially advantageous, where the gas is best permitted to diffuse of its own accord through a filter body to the
20 measurement position, so that it is not necessary for a gas sample to be sucked in with the aid of a pump. Such probes require little maintenance and deliver signals in short times which are favourable for automation purposes; due to the geometrical configuration of the filter - measurement cell arrangement it is possible according to requirements to achieve a spatial and chronological communication of the gas concentration values, which frequently fluctuate greatly in industrial gas currents. 20

25 Probes for oxygen measurement in flue gases have already been introduced in commerce. They contain galvanic cells with oxide ion-conducting solid electrolyte as a rule of stabilised zirconium dioxide; they are kept at the working temperature either by the surroundings or by an electric furnace.

In order to detect combustible gas constituents such as methane, carbon monoxide or hydrogen as well as oxygen, it was already proposed to measure the voltage between an electrode of Pt, Pd or Rh and an
30 electrode of Ag or Au, on oxide-ion conducting solid electrolytes. By reason of considerable differences in the catalytic activity of these electrodes, electric signals occur the magnitude of which increases with the concentration of the combustible gases. 30

It has further been proposed to separate off the oxygen from a chamber separated from the measurement gas chamber except for a narrow passage (capillary, gap or pores), by means of a galvanic cell through an
35 oxide-ion-conducting solid electrolyte, the time of flow of a constant current or the number of the necessary current pulses until practically complete oxygen separation being proportional to the oxygen concentration in the measurement gas. In this coulometric process no reference electrode is needed. 35

The possibility of impregnating porous inner bodies with electrolyte substances and using them for the assembly of solid electrolyte cells has long been known. Such cells with carbonate electrolyte and silver
40 electrodes have been proposed for the potentiometric determination of oxygen and carbon dioxide. 40

In more recent times it was proven that in oxygen-containing gases many gaseous anhydrides can be determined potentiometrically with cells which contain salts with oxide anions of the anhydrides as solid electrolytes. By way of example it appeared that on potassium sulphate as solid electrolyte and on
45 electrodes with platinum at 820°C, voltages of SO₂ concentration cells largely corresponding to Nernst's equation can be measured over a range from about 1 to 10,000 ppm.vol. Admittedly with sensors of this kind at the same time there is a dependence upon the quotient of the oxygen partial pressures present in the electrode chambers. The electrochemical gross electrode reactions and the cell reactions which can proceed in the gas sensors of special interest here are in fact the following:- 45

50 O₂ - Sensor
 $\frac{1}{2}O_2 + 2e^- \rightleftharpoons O^{2-}$ O₂(1) O₂(2) 50
SO₂ - Sensor
 $SO_2 + O_2 + 2e^- \rightleftharpoons SO_4^{2-}$ SO₂(1)+O₂(1) \rightleftharpoons SO₂(2) + O₂(2)
CO₂ - Sensor
55 CO₂ + $\frac{1}{2}O_2 + 2e^- \rightleftharpoons CO_3^{2-}$ CO₂(1)+ $\frac{1}{2}O_2$ (1) \rightleftharpoons CO₂(2) + $\frac{1}{2}O_2$ (2) 55
NO₂ - Sensor
NO₂ + $\frac{1}{2}O_2 + e^- \rightleftharpoons NO_3^-$ NO₂(1) + $\frac{1}{2}O_2$ (1) \rightleftharpoons NO₂(2) + $\frac{1}{2}O_2$ (2)

If the oxygen partial pressure in the measurement gas is equal to that in the reference gas, for example in
60 the case of trace measurements in air, then the influence of this pressure upon the cell voltage is emphasised. If the oxygen partial pressure in the measurement gas fluctuates greatly however, for example in the case of measurements in flue gases, it must be taken into consideration, for which purpose the combination of the signal of the SO₂ - , CO₂ - or NO₂ - sensor with the signal of an oxygen sensor was proposed. 60

reference electrodes of a metal and the corresponding salt of this metal can be used. If no reducing gas is acting, reference electrodes of silver and silver sulphate, carbonate or nitrate in solid solution in the solid electrolyte material are suitable.

The apparatuses proposed hitherto for gas analysis with solid electrolyte cells are very manifold as regards the nature and form of the solid electrolytes, the configuration of the electrodes, the use of reference systems, heating and filtering devices and the arrangement of these components. For every gas analysis process with solid electrolyte cells and for every type of solid electrolyte, special constructions have been indicated; on the other hand constructions of gas measurement probes which are multifunctionally usable are lacking.

Many special components and various kinds of arrangements are unfavourable for industrial series manufacture. The probes thus become expensive and cannot be used even in small industrial installations to the extent as desirable.

Many proposed apparatuses in fact fulfil their purpose in the condition immediately after production, but are not sufficiently stable in their mechanical and electrochemical properties to withstand the rough conditions of industrial use in the long term. Moreover many apparatuses proposed hitherto do not conform with the demands of simple secure fitting in industrial series manufacture; more especially simple secured electric supply leads to the measurement cell are often not guaranteed. Finally metallic components are frequently used where ceramic parts should better have been utilised to avoid corrosion.

The purpose of the invention is an apparatus which can easily be manufactured industrially and with minor variations of individual components and using many components already usual in commerce acts as relatively cheap, operationally reliable sensor with wide range of use for different individual gases or simultaneously for several different gases.

The invention is based upon the problem of indicating an apparatus of probe form having different solid electrolyte cells of as many ordinary commercial ceramic parts as possible, of which the solid electrolyte cells contain different ion conductors and electrode types and arrangements for known potentiometric, potentiometric-electro-catalytic, ammetric and coulometric processes, and can be inserted without substantial modification of the basic constructional conception in a simple and stable manner into the probe arrangement. The probe concept is to be usable for the determination of different gases singly or simultaneously over the entire temperature range in which the respective measurement principle and cell material are usable.

The invention is based upon a hollow body with ion conductivity or upon a hollow body containing parts with different ion conductivities, which body will hereinafter be called the basic body. The basic body externally carries a measurement electrode or several mutually separate measurement electrodes and internally contains a reference system or several reference systems lying opposite to different measurement electrodes. The cell arrangement according to the invention is now distinguished in that the lead wires to the individual electrodes are made fast on the basic body with the aid of passages through bores and of grooves on one end of the basic body and by a multiple capillary tube piece with bolt, and are secured with the aid of bends in the lead wires or corrosion-proof parts fitted on the lead wires against the action of traction and torsion upon the electrodes, and that the basic body with the electrodes and the attached leads is fitted to a gas-tight guide tube coaxially with the aid of a glass or a sintered composition, with gastight sealing of the wire passages, and is pushed together with the guide tube, with or without fitted-over electric furnace, temperature sensor and test gas conduit, into a porous ceramic tube acting as filter with closed or perforated end.

The leads from the measurement electrodes are laid through ceramic insulating tubes to the end of the basic body which abuts on the guide tube. There they are conducted through bores in the basic body perpendicularly of its axis in notches formed externally longitudinally of the basic body or at externally attenuated points into the interior of the basic body tube and then to the guide tube, the leads being bent at an angle of about 90° both before and after the bore.

The multiple capillary tube piece has on one end face a bolt which engages in a groove in the end face of the facing end of the basic body and prevents axial torsions. The electric leads of inner and outer electrodes are laid individually through the capillaries of the multiple capillary tube piece. On electric leads of inner electrodes, directly before the passage position through a capillary, there are bends or corrosion-proof parts made fast in any way which prevent pulling through the capillary. Directly behind the passage positions of electric leads through capillaries there are bends or corrosion-proof parts made fast in any way which prevent the exertion of pressure through leads upon electrodes.

To guarantee the gas-tight attachment of the basic body with the cell arrangement to the guide tube, these bodies and this tube should differ little from one another in coefficient of expansion; they are ground to fit to one another or otherwise deformed to fit and connected with a sealing composition the coefficient of expansion of which optimally lies between that of the basic body and that of the guide tube.

Parts of the basic body for the measurement of large to small oxygen partial pressures consist of an oxide-ion-conducting solid electrolyte primarily on the basis of stabilised zirconium dioxide. Parts of the basic body exclusively for the measurement of high oxygen partial pressures consist preferably of porous, electrically non-conductive, ceramic bodies in which the pores are impregnated with oxide-ion-conducting solid electrolytes with bismuth oxide as main constituent. Parts of the basic body for the measurement of the

preferably of porous, electrically non-conductive, ceramic bodies in which the pores are impregnated with salts the anions of which are capable of entering into an electrode reaction with the gaseous oxide to be detected analytically or with the gaseous oxide occurring by oxidation from the compound to be detected analytically, with exchange of electrons with the electrode metal and with oxygen from the measurement gas.

The measurement electrodes consist of porous layers of alloyed or unalloyed platinum metals with or without admixture of catalytically acting oxide substances or of porous layers of silver, gold or alloys thereof. For contacting, structures of wire, sheet metal or wire mesh preferably of the same noble metal are fitted thereon, to which electric leads in the form of scale-proof wires especially of Kanthal (Registered Trade Mark) are welded.

The reference electrodes in the interior of the tubular basic body are built up like the measurement electrodes or produced from an electron-conducting oxidic layer with contacting metallic structures and surrounded by a reference gas, especially air or air with specific content of SO_2 , NO_2 or CO_2 . The reference system for cells for the measurement of gaseous oxides internally on the ceramic body impregnated with pure salt can however also consist of a layer which is formed from the relevant salt with addition of a silver salt, a silver layer thereon and a contacting metallic structure thereon. In the case of such an apparatus the reference system is washed constantly with air against the danger of the action of oxygen-poor or reducing gases. Measurement gas chamber and reference electrode chamber are connected with one another through a capillary at the end of the basic body free from electric leads. As a result of negative pressure in the measurement gas chamber or due to a small excess pressure in the reference electrode chamber generated with suitable aids, reference or washing gas flows continuously over the reference electrodes through the capillaries into the measurement gas chamber.

For the execution of ammetric or coulometric methods the electrodes are formed with large areas and the outer electrode facing the measurement gas is surrounded by a tubular hollow body which is gas-tightly secured on the basic body on the side of the electric supply leads, by the use of sealing composition, and on the other side encloses the basic body except for a gas passage gap, the gas throughput of which can be limited by introduction of a porous cement.

The electric furnace for the heating of the solid electrolyte cells in the case of inadequate ambient temperatures consists of a ceramic tube with preferably 16 longitudinal bores in the tube wall. The heating conductor is conducted through 14 of these bores. The remaining bores lie opposite, accommodate the required number of thermo-couple elements and contain incisions and transverse bores for the passage of measurement gas.

For the setting of temperatures of different levels on different measurement electrodes these measurement electrodes are mounted in each case in the middle of different furnaces or at the positions in the temperature gradient of one furnace with the desired temperatures, and brought under control by suitably mounted thermo-couple elements.

The ceramic tube acting as filter and enclosing the mentioned probe parts possesses pores with width up to about $30\text{ }\mu\text{m}$, preferably of 5 to $10\text{ }\mu\text{m}$. Into the end of the unilaterally closed ceramic filter tube there is formed an opening for the pushing through of the reference gas exit capillaries. The ceramic filter tube is fitted for protection into a ceramic or scale-proof metal tube with gas conduit devices and gas passage openings and is installed therewith directly into the space with the gas for analysis or into an arrangement for the withdrawal of cross-sectional samples.

Where the gas flowing over the reference electrodes must not be admitted to the analysis gas chamber, the basic body is closed at the end without electric leads by a sealing composition, the filter tube is not perforated at the end and a tube for the forcing of gas into the reference electrode chamber is placed through a notch in the multiple capillary tube. The space within the ceramic filter tube around the measurement electrodes is limited to the side of the outflowing reference gas and to the opposite side by parts of ceramic or oxidic fibre material and sealed off extensively against dust.

The measurement electrodes are so enveloped by parts of the furnace or of ceramic tubes that suspended particles which have penetrated into the probe do not fall on to the measurement electrode, and measurement gas can diffuse to the measurement electrodes only by a horizontal path.

The free space between the measurement electrodes and the ceramic filter tube is filled out wholly or partially with loose pieces of 0.5 to 2.0 mm. thickness of gas-tightly sintered magnesium oxide or of stabilised zirconium oxide.

A multi-functional solid electrolyte gas sensor especially for measurements on flue gases of furnace installations is composed of a tube of oxidic solid electrolyte, externally with a measurement electrode of platinum (I) and one of gold (II) and internally with a reference electrode of platinum (III) lying opposite to I and II, and of a porous ceramic tube with potassium sulphate in the pores, externally with a measurement electrode of platinum (IV) and internally with a reference electrode (V) of potassium sulphate with 1% by mass silver sulphate and a layer of silver thereon. This combination of solid electrolyte cells is gas-tightly attached to a guide tube, internally contains pure air and is externally surrounded by an electric furnace and filter tube so that flue gas purified of dust can diffuse to the measurement electrodes I, II and IV. Electronic appliances are connected for oxygen measurement with the electrodes I and III for detection of unburnt gas constituents with the electrodes I and II and for the measurement of sulphur dioxide and trioxide with the electrodes III, IV and V in the manner suitable for the formation of the desired signals.

A mono-functional or multi-functional solid electrolyte gas sensor especially for transportable appliances for the measurement of gas partial pressures in the free atmosphere, on oxygen installations, in working premises, mine shafts etc., consists of largely miniaturised parts, especially of a basic body with external diameter of 2 to 3 mm., and is equipped with a micro-furnace which keeps the sensor at the working temperature with the aid of a transportable or cable-connected current source, and with a reference gas reservoir where the ambient air is not usable as reference gas.

At the points of entry of the gas for the reference system and of the test gas, replaceable gas filters and devices for the connection of suspended cone appliances (rotameters) for the constant or intermittent monitoring of the gas rate of flow are situated.

- 10 The embodiment of the basic body in accordance with the invention with the secured lead wires to the electrodes permits convenient fitting under normal conditions. The attachment to the guide tube and the sealing of all openings at this attachment point are achieved in one step at high temperature. The utilised parts and the indicated assembly offer essential advantages for a relatively simple series manufacture. The apparatus concept not only results in very variable possibilities of use, but also contains important prerequisites for a long life of the sensors in industrial gases:- Use of corrosion-proof ceramic parts, scale-proof lead wires welded to contact networks and leading without interruption out of the probe, dust retention by filters of small pore width and measurement gas chamber limitation, mounting of the measurement electrode protected against dust sedimentation in the filter chamber, absorbent and adsorbent media for contaminating vapours.

- 20 In the accompanying drawings:-

Figure 1 shows a plan view of a simple solid electrolyte cell with attached multiple capillary tube piece;
Figure 1a shows a plan view of the end of the multiple capillary tube piece facing the solid electrolyte tube;
Figure 1b shows a section through the multiple capillary tube piece;
Figure 2 shows a section through the simple solid electrolyte cell with attached multiple capillary tube

- 25 piece and part of the guide tube;

Figure 2a shows a section through a fitting of the solid electrolyte tube to the guide piece by grinding;

Figures 2b to 2f show sections and elevations of different devices which prevent movement of wires through the ceramic capillaries;

Figure 3 shows a section through a bi-functional arrangement on a solid electrolyte tube;

- 30 *Figure 4* shows a section through a solid electrolyte cell with large electrodes, hollow body enveloping the measurement electrode and attached parts;

Figure 5 shows a section through a tri-functional arrangement on two solid electrolyte tubes;

Figure 6 shows a section through the head of a probe with a simple solid electrolyte cell without heating furnace;

- 35 *Figure 7* shows a section through the head of a probe with bi-functional arrangement on a solid electrolyte tube in a heating furnace with gas passage openings in the middle part;

Figure 8 shows a section through a tube furnace for probe heating;

Figure 8a shows a plan view of an end face of the tube furnace before spreading with protective composition;

- 40 *Figure 9* shows a section through a simple solid electrolyte cell with return of the reference gas in a heating furnace with gas passage openings in the end part;

Figure 9a shows a plan view of the end of the multiple capillary tube facing the solid electrolyte tube, with lateral openings for the gas passage;

- 45 *Figure 10* shows a plan view of a probe with attachment piece and section through protective tube and installation position;

Figure 10a shows a plan view of the end of the probe.

The construction of a simple solid electrolyte cell with the solid electrolyte tube 1, the outer electrode 2, the inner electrode 10, the ceramic insulating tubes 3, the bore 6 in the notch 5 and with the electrode supply leads 4 and 11 fixedly mounted using the multiple capillary tube piece 7 is shown in plan view in *Figure 1* and turns through 90° after insertion into the guide tube 13 with the insulating tube 14 in section in *Figure 2*. The security against the action of traction, pressure or torsion upon the electrodes 2 and 10 by the lead wires 4 and 11 is achieved with the bends before and after the bore 6, with the three welded-on scale-proof metal plates 8 and with the bolt 9 (see *Figures 1a, 1b* and 2). Thus *Figure 1* shows a mechanically stable component which is attached by a single annealing process with the sealing composition 12 to the guide tube 13 in gas-tight manner. The stable seating of the solid electrolyte tube 1 in the guide tube 13 can be improved by a ground-in connection, for example as at 17 in *Figure 2a*. In place of the metal plates 8 it is also for example possible for scale-proof metal tubes 18 to be pushed over and pressed on or welded on (*Figure 2b*), doubly perforated ceramic plates 19 threaded through (*Figure 2c*), scale-proof metal plates 20 pressed out in the middle part can be pressed on (*Figure 2d*) or merely rounded portions (*Figure 2e*) or bent portions (*Figure 2f*) provided in the lead wires. Only after the connection of the solid electrolyte cell with the guide tube, after testing of the cell function and if necessary measures to improve the inner electrode, the capillary 15 with the sintered composition 16 is applied to the open end of the solid electrolyte tube.

For measurements of large to small oxygen partial pressures the solid electrolyte tube 1 consists of stabilised zirconium dioxide. For measurements on solid electrolytes which cannot alone be processed into

SiO₂ by mass, or from pure Al₂O₃ or MgO, is fitted to the guide tube and impregnated with one or more solid electrolyte materials, preferably in the fused condition. However it is also possible to use a gas-tight tube, for example of sintered corundum, with the necessary number of windows into which pure solid electrolyte bodies or porous ceramic bodies with solid electrolyte in the pores are inserted.

5 As sealing composition 12 for example between CaO-stabilised zirconium dioxide as solid electrolyte 1 and sintered corundum as guide tube 13, a mixture of a glass produced from 8 parts by mass of BaCO₃, 8 parts by mass of SiO₂ and one part by mass of Al₂O₃, and 5% by mass of finely pounded stabilised zirconium dioxide proves its value. For the production of the tube connection the arrangement is heated in the region of the sealing composition up to 1375° C. By substitution of a more or less large part of the BaCO₃ by CaCO₃ it is possible to vary the coefficient of expansion. The substantially greater thermal conductivity of sintered corundum over that of zirconium dioxide must be taken into account in that the temperature maximum of the furnace in the melting and cooling process is placed in the range of the sintered corundum tube.

The electrodes of the simple solid electrolyte cell are produced by application of a suspension of pure platinum particles of size $\leq 10 \mu\text{m}$ with additions of soluble pure alkali-free platinum compounds (up to 20% by mass of the metal content) in a viscous, well-drying, residue-freely burning organic liquid. After the annealing the layer should initially contain less than 5 mg/sq.cm. platinum, by repetition of the application 8 to 20 mg/sq.cm. platinum should be achieved. In order to improve the firmness of adhesion of the inner platinum layer it is advantageous to add 1 to 5% by mass of a glass as free as possible from alkali to the platinum for this layer. The porous platinum layers are contacted with platinum wire meshes to which the 20 "Kanthal" wires are welded. The layers can be loosened up by about 10 minutes long treatment of the cell between 800 and 1100° C. with alternating current of a current density between 0.2 and 1.5 A/sq.cm. in air before and repeatedly during the long-term operation, and thus the response rate of the electrodes can be improved.

It can be seen from Figure 3 that the construction simply permits of fitting a second outer electrode 21 and laying a lead wire 22 from it to the interior of the guide tube 13 in gas-tight manner with the multiple capillary tube 23. The electrode 21 is produced for example with gold, electrode 2 and the common reference electrode 10 with platinum. Then on a solid electrolyte tube of stabilised zirconium dioxide the oxygen partial pressure can be ascertained from the voltage between 2 and 10 and with the voltage between 2 and 21 the presence of combustible substances beside oxygen can be substantiated.

30 The examples described hitherto are intended for potentiometric measurements. For ammetric and coulometric analytical processes it is expedient to enlarge the electrodes as shown by Figure 4 with the measurement electrode 24 and the counter-electrode 25. In order to obtain a limit current proportional to the determining gas concentration or in order to be able to determine the gas concentration of the repeated extensive separation of the gas from a gas sample, a volume is limited off from the measurement gas with the hollow body 26. The tubular hollow body 26 is attached gas-tightly with the aid of the sealing composition 12 to a collar 27 of the guide tube 13. A continuous gas exchange takes place by way of the annular gap 28 which can be constricted in permeability with porous material. Either one measures the limit current flowing when constant voltage is applied, or by way of time and current one ascertains the charge which is necessary for the extensive separation of the gas after a period of complete concentration equalisation. In comparison with potentiometric methods the advantages exist that one obtains directly signals proportional to the gas concentration and that it is even possible to work without reference gas with the counter-electrode under measurement gas. The last-mentioned advantage is not exploited in the example as illustrated in Figure 4; instead here a stabilisation of the counter-electrode is achieved by constant air washing or by standing under the separated oxygen with sealing of the solid electrolyte tube on the one or the other side. The necessity of calibration of each such measurement arrangement is disadvantageous in comparison with potentiometric methods.

The number of measurement functions of a probe can be increased if as shown for example by Figure 5 a different kind of solid electrolyte tube 29 is attached in gas-tight manner with the sealing composition 30 to a solid electrolyte tube 1. The arrangements on the solid electrolyte tube 1 can correspond for example to those in Figure 3; the lead wires to one of the outer electrodes and to the air reference electrode are admittedly not visible in the section represented in Figure 5. The solid electrolyte tube 29 can be a porous ceramic tube produced from 80% Al₂O₃ and 20% SiO₂ by mass, with K₂SO₄ in the pores. The reference electrode in this tube then optimally consists of a layer 31 of K₂SO₄ with 1% Ag₂SO₄ by mass and thereupon a layer of pure silver which is contacted with a silver mesh 32 on the lead wire 33. To prevent the destruction of this reference electrode by reduction it is important that the air current over the reference electrode in the solid electrolyte tube 1 at the same time washes constantly over the reference electrode in the solid electrolyte tube 29.

The arrangement of the solid electrolyte cells, attached to the guide tube, in a porous ceramic tube 34 which at the same time acts as filter tube and carrier tube is shown by Figures 6 and 7. In Figure 6 there is illustrated a simple solid electrolyte cell without heating furnace in a support tube 35 with the blocking discs 36, 37, 38 and 39, the jacket thermo-couple element 40 and the test gas conduit 41. The support tube 35 is porous and moreover has incisions on one side for the gas passage. In Figure 7 there is illustrated a bi-functional arrangement corresponding to Figure 3 in a heating furnace 42 of tube form with incisions in the middle zone. As well as the jacket thermo-couple 40 for the one measurement electrode 2 a second jacket

temperature maximum. The jacket thermo-couple elements are secured together with the test gas conduit 41 and the current leads of the heating furnace in the ceramic insulating tube 44 on the guide tube 13 with a tie piece 45. The blocking discs 37, 38 and 39, the asbestos filaments 46 and 47 fitted in grooves of the heating furnace body, the support tubes 48 and 49 and asbestos wool 50, which can further be covered with a closure composition 51, ensure the limitation of the measurement gas chamber. For the filter and carrier tube 34 there is used for example an ordinary commercial, unilaterally closed ceramic tube produced from 80% Al_2O_3 and 20% SiO_2 by mass, with pores predominantly of width 5 to 10 μm , into the end of which a bore is formed.

In order to prolong the working time of the probes by keeping away contaminants of vapour form, the free space around the measurement electrodes is filled with loose pieces of 0.5 to 2.0 mm. thickness of gas-tightly sintered stabilised zirconium dioxide as adsorbent or absorbent agent. The pieces must be not too fine and not porous, in order to avoid inertia of the probe due to the adsorption and desorption of analysis gas.

The heating furnace 42 is represented in greater detail in section in Figure 8 and in plan view of one end face in Figure 8a. In Figure 8a there may be seen the transferences of the heating coils between the bores, where 2 of 16 bores remain free. The transferences of the heating coils lying sunk in a channel are spread over with a protective composition on both sides.

Figure 9 shows the longitudinal section through the heating furnace perpendicularly of that in Figure 8, where as in Figure 7 the bores remaining free from the heating coil are visible. In departure from Figure 7, in Figure 9 gas passage openings are represented in the end zone of the furnace. The illustrated cell has a solid electrolyte tube closed at one end with a sealing composition 52. In this case the reference gas is supplied through a gas conduit 53 and flows away backwards into the guide tube 13. Figure 9a shows the necessary modifications to the multiple capillary tube piece 54 in order that the gas conduit may be fitted and to render possible the gas return flow (see Figure 1a). If the gas conduit tube 53 is provided from the same corrosion-proof metal as the jacket of the thermo-couple elements 40, then the two tubes can also be used as electric leads to the inner and outer electrodes.

Finally the installation of a probe with attachment piece into the wall 55 of an analysis gas chamber may be seen from Figure 10. The securing for example simply with a cap nut 56 is possible. The probe is pushed into the protective tube 57, for example of sicromal steel, with incisions 58 and gas-conductor devices 59 to improve the gas washing and the keeping away of flue dust. Figure 10a illustrates the incisions and the gas-conductor device in plan view of the end of the probe.

CLAIMS

1. Apparatus for gas analysis with galvanic solid electrolyte cells which contains as cell arrangement a hollow body with ion conductivity and electrodes, with an electric furnace optionally situated around the hollow body in the region of the electrodes, utilising potentiometric, ammetric and coulometric measurement methods and utilising catalytic effects, characterised in that the hollow body, which can also possess different ion conductivity - hereinafter called basic body - externally possesses several mutually separate measurement electrodes and in this basic body there are situated a reference system or several reference systems situated opposite to different measurement electrodes, the lead wires to the individual electrodes are fastened on the basic body with the aid of grooves and passages through bores at one end of the basic body and are secured against traction, pressure and torsion by a multiple capillary tube piece with bolt or corrosion-proof parts fitted on the lead wires, and in that the basic body with the electrodes and the attached leads is fitted in gas-tight manner coaxially with the aid of a glass or a sintered composition to a gas-tight guide tube and pushed together with the guide tube, with temperature sensor and test gas conduit, into a porous ceramic tube, acting as filter, with closed or perforated end.

2. Apparatus as claimed in Claim 1, wherein the leads are laid from the measurement electrodes to the end of the basic body which adjoins the gas-tight guide tube, in that there they are conducted through bores in the basic body perpendicularly of its axis in notches fitted externally along the basic body or on externally attenuated parts into the interior of the basic body tube and then to the guide tube, the leads being bent through an angle of about 90° before and after the bore.

3. Apparatus as claimed in Claims 1 and 2, wherein the multiple capillary tube piece has on one end face a bolt which engages in grooves in the end face of the facing end of the basic body, in that the electric leads of inner and outer electrodes are laid singly through the capillaries of the multiple capillary tube piece, in that bent portions or secured corrosion-proof parts are situated on electric leads of inner electrodes directly before the point of passage through a capillary and in that bent portions or secured corrosion-proof parts are situated directly behind the passage points of electric leads through capillaries.

4. Apparatus as claimed in Claims 1 to 3, wherein the basic body and the guide tube differ only slightly from one another in coefficient of expansion, are ground to fit one another or otherwise deformed to fit and are connected with a sealing composition the coefficient of expansion of which lies preferably between that of the basic body and that of the guide tube.

5. Apparatus as claimed in Claims 1 to 4, wherein parts of the basic body for the measurement of large to small oxygen partial pressures consist of an oxide-ion-conducting solid electrolyte preferably on the basis of

- partial pressures consist preferably of porous, electrically non-conductive ceramic bodies in which the pores are impregnated with oxide-iron-conductive solid electrolytes with bismuth oxide as main constituent and in that parts of the basic body for the measurement of the partial pressures of sulphur-containing, nitrogen-oxide-containing or carbon-containing gases are assembled preferably from porous, electrically non-conductive ceramic bodies in which the pores are impregnated with salts the anions of which are capable of entering into an electrode reaction with the gaseous oxide to be detected analytically or with the gaseous oxide produced by oxidation from the compound to be detected analytically, electrons being exchanged with the electrode metal, and with oxygen from the measurement gas. 5
6. Apparatus as claimed in Claims 1 to 5, wherein the measurement electrodes consist of porous layers of alloyed or unalloyed platinum metals with or without admixture of oxidic substances or of porous layers of silver, gold or alloys thereof, and in that for contacting, structures of wire, sheet metal or wire mesh preferably of the same noble metal are applied thereto, to which electric leads in the form of scale-proof wires are welded. 10
7. Apparatus as claimed in Claims 1 to 6, wherein the reference electrodes in the interior of the tubular basic body are built up like the measurement electrodes or produced from an electron-conductive oxidic layer with contacting metallic structures and are surrounded by a reference gas, preferably air or air with a specific content of SO_2 , NO_2 or CO_2 . 15
8. Apparatus as claimed in Claims 1 to 6, wherein the reference system for cells for the measurement of gaseous oxides consists internally on the ceramic body impregnated with pure salt of a layer formed from the relevant salt with addition of a silver salt, a silver layer thereon and a contacting metallic structure thereon, and is constantly washed over with air. 20
9. Apparatus as claimed in Claims 1 to 8, wherein the measurement gas chamber and reference electrode chamber are connected with one another through a capillary at the end of the basic body free from electric leads. 25
10. Apparatus as claimed in Claims 1 to 9, wherein for carrying out ammetric or coulometric measurement methods the electrodes are made with large area and the outer electrode facing the measurement gas is surrounded by a tubular hollow body which is gas-tightly secured on the basic body on the side of the electric supply leads by the use of sealing composition, and on the other side encloses the basic body except for a gas passage gap, the gas passage of which can be constricted by introduction of a porous cement. 30
11. Apparatus as claimed in Claims 1 to 10, wherein the electric furnace for the heating of the solid electrolyte cells in the case of inadequate ambient temperatures consists of a ceramic tube especially with longitudinal bores in the tube wall, in that the heating conductor is conducted through 14 of these bores, in that the remaining bores lie opposite to one another and accommodate the required number of thermo-couple elements and in that incisions and transverse bores for the passage of measurement gas are formed in the two bores without heating conductors. 35
12. Apparatus as claimed in Claims 1 to 11, wherein for the establishment of different temperature levels on different measurement electrodes these are mounted each in the middle of different furnaces or at positions in the temperature gradient of one furnace with the desired temperatures, and are brought under control by appropriately mounted thermo-couple elements (40, 43). 40
13. Apparatus as claimed in Claims 1 to 12, wherein the ceramic tube acting as filter and enclosing the stated probe parts possesses pores with widths up to $30\text{ }\mu\text{m}$, preferably from $5\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$, in that into the end of the unilaterally closed ceramic filter tube there is formed an opening for the pushing through of the reference gas exit capillaries, in that the ceramic filter tube is fitted for protection in a ceramic tube or scale-proof metal tube with gas-conductor devices and gas passage openings and installed therewith directly into the chamber with the analysis gas or into an arrangement for the extraction of cross-sectional samples. 45
14. Apparatus as claimed in Claims 1 to 8 and 10 to 13, wherein where it is not permissible to emit the gas flowing over the reference electrodes into the analysis gas chamber, the basic body is closed at the end without electric leads by a sealing composition, the filter tube is not perforated at the end and a tube for the forcing of gas into the reference electrode chamber is laid through a notch in the multiple capillary tube. 50
15. Apparatus as claimed in Claims 1 to 14, wherein the space within the ceramic filter tube around the measurement electrodes is limited and largely sealed off against dust towards the side of the outflowing reference gas and towards the opposite side by parts of ceramic material or oxidic fibre material. 55
16. Apparatus as claimed in Claims 1 to 15, wherein the measurement electrodes are enveloped by parts of the furnace or of ceramic tubes in such a way that suspended particles which have penetrated into the probe do not drop on to the measurement electrode and measurement gas can diffuse to the measurement electrodes only by a horizontal path. 60
17. Apparatus as claimed in Claims 1 to 16, wherein the free space between the measurement electrodes and the ceramic filter tube is wholly or partially filled out with loose pieces of $0.5\text{ to }2.0\text{ mm}$ thickness of gas-tightly sintered magnesium oxide or of stabilised zirconium dioxide. 65
18. Apparatus as claimed in Claims 1 to 6, 8, 9, 11 to 13, 15 to 17, wherein a multi-functional solid electrolyte gas sensor especially for measurements on flue gases of furnace installations is composed of a tube of oxidic solid electrolyte, externally with a measurement electrode of platinum and a measurement

ceramic tube with potassium sulphate in the pores, externally with a measurement electrode of platinum and internally with a reference electrode of potassium sulphate with 1% by mass of silver sulphate and a layer of silver thereon, in that this arrangement of solid electrolyte tube cells is gas-tightly attached to a guide tube, internally contains pure air and externally is surrounded by an electric furnace and filter tube so
5 that flue gas purified of dust can diffuse to the measurement electrodes, and in that electronic appliances for oxygen measurement are connected with the electrodes, for detecting unburnt gas constituents with electrodes and for the measurement of sulphur dioxide and trioxide with the electrodes, in the manner suitable for the formation of the desired signals.

19. Apparatus as claimed in Claims 1 to 15, wherein a mono-functional or multi-functional solid
10 electrolyte gas sensor especially for transportable appliances for the measurement of gas partial pressures in the free atmosphere, on oxygen installations, in working premises, mine shafts, etc., consists of largely miniaturised parts, especially with a basic body with 2 to 3 mm. external diameter, and is equipped with a micro-furnace which keeps the sensor at the working temperature with the aid of a transportable current source, and with a reference gas reservoir where the ambient air is not usable as reference gas.

15 20. Apparatus as claimed in Claims 1 to 19, wherein at the entry points of the gas for the reference system and of the test gas there are situated replaceable gas filters and devices for the attachment of suspended cone appliances (rotameters) for the constant or intermittent monitoring of the gas rate of flow.

21. A gas analyser substantially as described with reference to the accompanying drawings.

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